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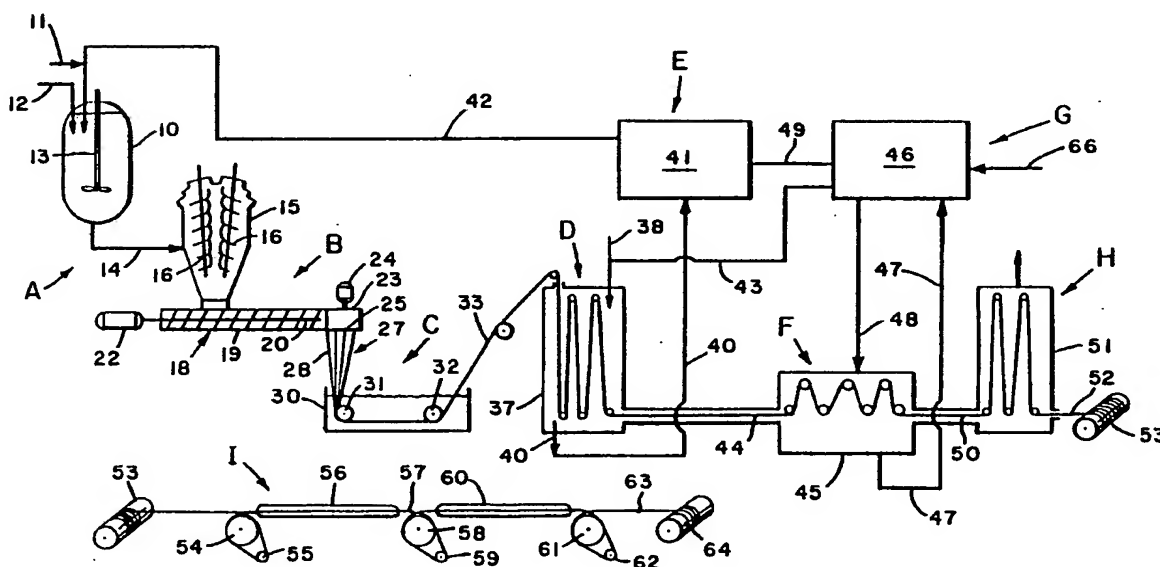
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(54) Title: METHOD FOR REMOVAL OF SPINNING SOLVENT FROM SPUN FIBER



(57) Abstract

The invention relates to a process for removal of spinning solvents from solution spun fibers by extraction with an extraction solvent such as a polyether.

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**METHOD FOR REMOVAL OF
SPINNING SOLVENT FROM SPUN FIBER**

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BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a process for removal of spinning solvents from solution spun fibers. More particularly, this invention relates to a process for extraction of a spinning solvent from solution spun fiber in which the solution is spun into a coagulation or gelation liquid.

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2. Prior Art

The preparation of fibers through gel spinning and solution spinning process are known. For example, U.S. Patent Nos. 4,413,110, 4,455,273, 4,536,536, 4,551,296; 20 4,440,711; 4,713,290; 4,883,628; 4,771,616; 2,509,279 and 4,334,102; Polymer Bulletin, vol. 1, pp. 879-80 (1979); Polymer, 2584-90 (1980); Polymer Bull., vol. 2, pp. 775-83 (1980); Soc Chem Ind, London, Monograph No. 30, pp. 188-207 (1968); Applied Polymer Symposia, no. 25 6, pp. 109-49 (1967); German Offen 3004699 (August 21, 1980); UK Application 2,051,667 (January 21, 1981); Polymer Bulletin, vol. 1, pp. 879-880 (1979) and vol. 2, pp. 775-83 (1980); and Polymer 2584-909 1980).

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SUMMARY OF THE INVENTION

One aspect of this invention relates to a process of extracting a material from a fiber which comprises the steps of:

- (a) extracting a continuous length of a fiber containing a first spinning solvent with a second extraction solvent for a sufficient contact time to

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form a solution of said extracted first spinning solvent and said second extraction solvent and a fiber containing said extraction second solvent, which fiber is free or substantially free of said first solvent and of substantially indefinite length; wherein said second extraction solvent is selected from the group consisting of :

- (i) a second extraction solvent in which said first spinning solvent is soluble or substantially soluble at a first temperature, T_1 , and is insoluble or substantially insoluble at a second temperature, T_2 , such that said second extraction solvent is capable of extracting said first spinning solvent from said fiber at said first temperature, T_1 , to form a first solution comprising said first spinning solvent and said second extraction solvent and such that on subjection of said first solution to said second temperature T_2 , a first heterogenous mixture is formed comprising two distinct liquid phases, a first liquid phase comprising predominantly said first spinning solvent and a second liquid phase comprising predominantly said second extraction solvent; and
- (ii) a second extraction solvent in which said first spinning solvent is soluble or substantially soluble, which second extraction solvent is soluble or substantially soluble in a third extraction solvent which is immiscible in said first spinning solvent, said relative solubility of said second extraction solvent in said first spinning solvent and in said third extraction

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solvent being such that said third extraction solvent is capable of extracting all or a portion of said second extraction solvent from a second solution comprising said second extraction solvent and said spinning solvent to form a second heterogeneous liquid mixture comprising two distinct liquid phases, a third liquid phase comprising predominantly said first spinning solvent and a fourth liquid phase comprising predominantly said second extraction solvent and said third extraction solvent;

(b) separating said first solution or said second solution into said first and second liquid phases by subjecting said first solution to said second temperature, T_2 , for a time sufficient to form said first heterogeneous mixture or by extracting said second solution with said third extraction solvent for a time sufficient to form said second heterogeneous liquid mixture; and

(c) recycling said second phase or said fourth phase to said extraction step.

Yet another aspect of this invention relates to an improved gel spinning process of the type which comprises the steps of forming a solution of a polymer of fiber forming molecular weight in a first spinning solvent; extruding said solution through an aperture, said solution being at a spinning temperature upstream of said aperture which is greater than the temperature at which a rubbery gel forms and being substantially at the first concentration both upstream and downstream of said aperture; cooling the solution adjacent to and downstream of the aperture to a second temperature below the temperature at which a rubbery gel is formed, forming a gel containing first solvent of substantially

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indefinite length; extracting the gel containing said first solvent with a second solvent for a sufficient contact time to form a fibrous structure containing said second solvent, which structure is substantially free of said first solvent and is of substantially indefinite length; drying the fibrous structure containing said second solvent to form a xerogel of substantially indefinite length free of said first and second solvent; and stretching at least one of the gel containing the first solvent, the fibrous structure containing the second solvent and the xerogel, the improvement comprising the steps of;

(a) extracting a continuous length of a fiber containing a first spinning solvent with a second extraction solvent for a sufficient contact time to form a solution of said extracted first spinning solvent in said second extraction solvent and a fiber containing said extraction second solvent, which fiber is free or substantially free of said first solvent and of substantially indefinite length; wherein said second extraction solvent is selected from the group consisting of :

(i) a second extraction solvent in which said first spinning solvent is soluble or substantially soluble at a first temperature, T_1 , and is insoluble or substantially insoluble at a second temperature, T_2 , such that said second extraction solvent is capable of extracting said first spinning solvent from said fiber at said first temperature, T_1 , to form a first solution comprising said first spinning solvent and said second extraction solvent and such that on subjection of said first solution to said second temperature T_2 , a first heterogenous

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mixture is formed comprising two distinct liquid phases, a first liquid phase comprising predominantly said first spinning solvent and a second liquid phase comprising predominantly said second extraction solvent; and

5 (ii) a second extraction solvent in which said first spinning solvent is soluble or substantially soluble, which second
10 extraction solvent is soluble or substantially soluble in a third extraction solvent which is immiscible in said first spinning solvent, said relative solubility of
15 said second extraction solvent in said first spinning solvent and in said third extraction solvent being such that said third extraction solvent is capable of extracting all or a
20 portion of said second extraction solvent from a second solution comprising said second extraction solvent and said spinning solvent to form a second heterogeneous liquid mixture comprising two distinct liquid phases, a
25 third liquid phase comprising predominantly said first spinning solvent and a fourth liquid phase comprising predominantly said second extraction solvent and said third extraction solvent;

(b) separating said first solution or said second solution into said first and second liquid phases by
30 subjecting said first solution to said second temperature, T_2 , for a time sufficient to form said first heterogeneous mixture or by extracting said second solution with said third extraction solvent for a time sufficient to form said second heterogeneous
35 liquid mixture; and

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(c) recycling said second phase or said fourth phase to said extraction step.

BRIEF DESCRIPTION OF THE DRAWINGS

5 The invention will be more fully understood and further advantages will become apparent when reference is made to the following detailed description of the invention and the accompanying drawing which is a schematic illustration of preferred embodiments of this
10 invention.

DETAILED DESCRIPTION OF THE INVENTION

In the broadest aspects, this invention relates to a process for extracting the spinning solvent from
15 polymeric fiber spun from a solution of a polymer in the solvent. In this process, a continuous length of fiber containing a first spinning solvent is contacted with a second extraction solvent which is a non-solvent for said polymer of the fiber to form a mixture or
20 solution of the two solvents. As used herein, a fiber is an elongated body, the length dimension of which is much greater than the dimensions of width and thickness. Accordingly, the term fiber includes a yarn, thread, filaments, both multifilament and
25 monofilaments, ends of yarn containing multiple filaments, tapes, ribbons, strips and the like having regular or irregular cross-sections. As used herein, "solvent" shall mean a fluid that is liquid under process conditions and which will extract or remove in
30 any manner that spinning liquid from the solution spun fiber.

Means for contacting the spinning containing fiber with the extracting solvent is not critical, any conventional solvent extracting means can be used. For
35 example, the extracting solvent and fiber can be

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contacted by counter current techniques or co-current techniques. In the preferred embodiments of the invention, the extracting solvent and the fiber containing the spinning solvent are contacted using the apparatus and method of U.S. Patent No. 4,771,616.

The extracting solvent and the fiber containing the spinning solvent are contacted for a time sufficient to extract all or substantially all of the spinning solvent from the fiber and to replace it with the second extraction solvent. In general, the residual amount of spinning solvent remaining in the fiber after extraction is at most about 15% by weight of fiber. More preferably the amount of residual spinning solvent is less than about 5% by weight, and most preferably is less than about 1.5% by weight of the fiber.

Extraction times may vary widely and are such that the desired amount of spinning solvent is extracted. Extraction times will depend on a number of factors as for example the extraction temperature, the solubility of the spinning solvent in the extracting solvent and the like. Usually, extraction times will vary from a few minutes or seconds up to hours or days. Preferred extraction times are from about 30 seconds to about 24 hours, more preferred extraction times are from about 30 seconds to about 30 minutes and most preferred extraction times are from about 30 seconds to about 10 minutes.

Useful extraction temperatures vary widely depending on a number of factors, in particular the solubility of the spinning solvent in the extraction solvent at a given temperature. Preferably, the extraction step is carried out at ambient temperature, i.e., from about 20°C to about 30°C.

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The number of contacts may vary widely and will depend to a significant extent on the mutual solubilities of the first spinning solvent and the second extraction solvent at the contacting temperature. For example, in those instances where the mutual solubility and fiber porosity are high and the amount of spinning solvent contained in the fiber is low, the desired amount of spinning solvent may be removed in as few as one contacting cycle. However, on the other hand where mutual solubilities and fiber porosities are low and the amount of spinning solvent in the fiber is high, more than one contact cycle may be required to extract the desired amount of spinning solvents from the fiber. In general, the contacting times and cycles are selected such that the residual spinning solvent remaining in the fiber is at the desired amount, preferably not more than about 5% by weight of the fiber and most preferably not more than about 1.5% by weight of the fiber.

The second extraction solvent may vary widely provided that it is a solvent for the spinning solvent and is capable of extracting the desired amount of spinning solvent from the fiber, preferably all or substantially all, of the spinning solvent from the fiber. The first extraction solvent also is preferably such that the first spinning solvent can be separated from the extraction solvent for recycling. In one preferred embodiment of the invention, the second extraction solvent is a solvent for the spinning solvent at temperature, and is soluble in a third extraction solvent which is not soluble in the spinning solvent and has relative solubility in said spinning solvent and said third extraction solvent such that said third extraction solvent is capable of extracting the second extraction solvent from a solution.

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comprising the spinning solvent and the second extraction solvent. In this preferred embodiment of the invention, the spinning and the third extraction solvents can be separated by solvent extraction.

5 In another preferred embodiment of the invention, the second extraction solvent is a solvent for the first spinning solvent at a first temperature, T_1 , is a non-solvent for the first spinning solvent at a second temperature, T_2 ; is a non-solvent for the polymer
10 forming the fiber at both the first temperature, T_1 , and the second temperature, T_2 ; and has a boiling point at 760 mm of Hg greater than the highest temperature used in the conduct of the extraction process. In this
15 embodiment of the invention, the second extraction and the first spinning solvents can be separated by varying the temperature of the spinning and extraction solvent solution.

Extraction solvents having the desired characteristics can be identified through use of
20 solubility and boiling point studies. The extraction solvent will depend to the most significant extent on the spinning solvent. The spinning solvent will vary depending on the polymer forming the fibers. For example, in those instances where the fiber is formed
25 from poly(vinyl alcohol) the spinning solvent is preferably aliphatic and aromatic alcohols such as hydrocarbon polyols and alkylene ether polyols having a boiling point (at 101 kPa) between about 150°C and 300°C. Such solvents include ethylene glycol,
30 glycerin, propylene glycol, glycerol, diethylene glycol and trimethylene glycol. In those instances where the fiber is formed from poly(acrylonitrile), useful spinning solvents include dimethyl sulfoxide, dimethyl formamide, and the like. Similarly, where the polymer
35 forming the fiber is a polyolefin, such poly(ethylene),

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poly(propylene) and copolymers of ethylene and propylene, spinning solvents are preferably aliphatic and aromatic hydrocarbons such as mineral oil, paraffin oil, decalin, poly(ethylene) wax and mixtures thereof.

5 In these instances, useful extractive solvents having the desired characteristics may be identified through routine temperature/solubility studies. For example, in the preferred embodiments of the invention where the fiber is formed from a polyolefin (preferably
10 poly(ethylene) and where the spinning solvent is a hydrocarbon preferably mineral oil, paraffin oil or decalin the extraction solvents are preferably polyether solvents such as diethylene glycol monobutyl ether and diethylene glycol monopropyl ether.

15 In addition to the essential boiling point and solubility characteristics, the extraction solvents for use in the preferred embodiments of the invention also exhibit a flash point (open cup) equal to or greater than about 87.8°C; boiling point at 760 mm of Hg equal
20 to or greater than about 190°C; a vapor pressure at 25°C equal to or less than about 0.4mm of Hg and no chlorine atoms in the solvent structure.

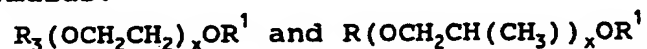
More preferred extraction solvents are polyether solvents. Useful polyether solvents are described in
25 U.S. Patent No. 3,737,392.

Preferred polyether solvents are monoalkyl or dialkyl ethers of polyalkylene glycols with alkyl groups of 1 to about 5 carbon atoms (especially methyl and ethyl) and alkylene groups of 2 to about 6 carbon
30 atoms (especially ethylene) and polyalkylene glycol groups with alkylene moieties of 2 to about 6 carbon atoms. Illustrative of such preferred solvents are poly(propylene glycol) molecular weight from about 425 to about 1200), tetraethylene glycol dimethyl
35 ether(tetraglyme), triethylene glycol dimethyl

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ether(triglyme), diethylene glycol dimethyl ether(diglyme), diethylene glycol monobutyl ether, diethylene glycol monoethyl ether, tripropylene glycol, diethylene glycol monomethyl ether, diethylene glycol divinyl ether, diethylene glycol monoisobutyl ether, diethylene glycol dibutyl ether, diethylene glycol monopropyl ether, triethylene glycol, tetraethylene glycol, diethylene glycol tert-butyl methyl ether, diethylene glycol diethyl ether, and propylene glycol monomethyl ether.

Preferred groups of polyether solvents are polyethylene glycol ethers and polypropylene glycol ethers of the formulas:



wherein x is an integer from 1 to about 8, and R and R¹ are the same or different and are hydrogen or alkyl having from 1 to about 4 carbon atoms; and mixtures of such glycol ethers. More preferred polyether solvents are polyethylene glycol ethers of the formula:



wherein X is an interger of from about 2 to about 5, and R and R¹ are the same or different and are hydrogen, methyl, ethyl, propyl or butyl, preferably with the proviso that at least one of R and R¹ is other than hydrogen. Most preferred solvents are tetraethylene glycol dimethyl ether, triethylene glycol dimethyl ether, diethylene glycol monobutyl ether and diethylene glycol mono propyl ether, with diethylene glycol mono butyl ether and diethylene glycol mono propyl ether being the solvents of choice.

Useful preferred polyether solvents may be prepared by conventional methods such as by acid catalyzed polymerization of propylene oxide, ethylene oxide and mixtures of propylene oxide and ethylene oxide. Such solvents may also be obtained from

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commercial sources. For example, such materials can be obtained from Wyandotte Corporation under the tradename Pluracol polyethylene glycol E 200, E 300, E 400 and E 600 and Pluracol poly propylene glycol P 410; and from
5 Dow Corporation under the tradename Polyglycol P 400. Also, glycol ethers may be obtained from Eastman Kodak e.g. EKTASOLV DP and EKTASOLV DB, from Union Carbide e.g. Butyl CARBITOL and from Oxy Chem e.g. diethylene glycol DB and diethylene glycol HB Tetraglyme may be
10 obtained from Ferro Corp.

The polymer for the fiber may vary widely, the only requirement is that the polymer is soluble in spinning solvent and insoluble in the extraction solvent. Illustrative of useful polymers are
15 polyamides and their copolymers such as poly(metaphenylene isophthalamide), poly(p-phenylene terephthalamide), copolyamide of 30% hexamethylene diammonium isophthalate and 70% hexamethylene diammonium adipate, copolyamide of 30%
20 bis(amidocyclohexyl) methylene, terephthalic acid and caprolactam, poly (hexamethylene adipamide) (nylon 66), poly(6-aminohexanoic acid) (nylon 6), poly(11-amino-undecanoic acid) (nylon 11), poly(hexamethylene sebacamide) (nylon 6,10) and the like; polymers and
25 copolymers formed by the polymerization of α , β -unsaturated olefins such as poly(acrylonitrile), poly(vinyl alcohol), poly(acrylic acid), polyolefins as for example poly(ethylene) and poly(propylene), copolymers of vinyl acetate and vinyl chloride; and
30 polyesters such as poly(butylene terephthalate), poly(ethylene terephthalate) and poly(1,4-cyclohexane dimethylene terephthalate). Preferred polymers are polyamides and polymers of α , β -unsaturated monomers such as polyolefins (especially poly(propylene) and
35 poly (ethylene), poly (vinyl alcohol) and

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poly(acrylonitrile).

Poly(ethylene) is the polymer of choice. As used herein, the term "poly(ethylene)" shall mean a predominantly linear poly(ethylene) material that may contain minor amounts of chain branching or comonomers not exceeding 5 modifying units per 100 main chain carbon atoms, and that may also contain admixed therewith not more than about 50 wt% of one or more polymeric additives such as alkene-1-polymers, in particular low density poly(ethylene), poly(propylene) or poly(butylene), copolymers containing mono-olefins as primary monomers, oxidized polyolefins, graft polyolefin copolymers and polyoxymethylenes, or low molecular weight additives such as anti-oxidants, lubricants, ultra-violet screening agents, colorants and the like which are commonly incorporated by reference.

The polymers are of fiber forming molecular weight. Such molecular weights for the various fiber forming polymers as well known in the art and will not be described in great detail. For example, in the case of preferred poly(ethylene), poly(propylene), poly(acrylonitrile) and poly(vinyl alcohol), suitable polymers are those having a molecular weight of at least about 150,000, preferably at least about 1,000,000, more preferably from about 1,000,000 to about 5,000,000 and most preferably from about 2,000,000 to about 5,000,000.

Solvent containing fibers for use in this invention can be conveniently prepared by gel or solution spinning techniques. Illustrative of such procedures are those described in U.S. Patent Nos. 4,457,985; 4,137,394; 4,356,138; 4,440,711; 4,713,290; 4,551,296; 4,599,276 and 4,535,027, German Off. 3,004,699, GB 2051667; and EPA 64,167 all of which are

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hereby incorporated by reference. Accordingly, these processes will not be described in any great detail. Of these processes, fibers formed by the spinning processes of U.S. Patent Nos. 4,413,110, 4,455,273, 5 4,536,536, 4,551,296, 4,440,771, 4,713,290 and 4,883,628 are preferred.

In these preferred processes, a suitable polymer is dissolved in a suitable non-volatile solvent usually in an amount of from about 5 to about 15% by weight of 10 the solution, preferably from about 4 to about 10% by weight of the solution.

The fiber containing the spinning solution is extruded through a spinning aperture at a temperature no less than a first temperature upstream of the 15 aperture at substantially the same concentration upstream and downstream of the aperture and cooling the solution adjacent to and downstream of the aperture to a second temperature below the temperature at which a rubbery gel is formed, forming a gel containing the 20 spinning solvent of substantially indefinite length.

The first solvent should be relatively non-volatile under the processing conditions. This is necessary in order to maintain essentially constant concentration of solvent upstream and through the 25 aperture (die) and to prevent non-uniformity in liquid content of the gel fiber or film containing first solvent. Preferably, the vapor pressure of the first solvent should be no more than 80 kPa (four-fifths of an atmosphere) at 180°C, or at the first temperature. 30 Suitable first spinning solvents for useful polymers as for example poly(ethylene), poly(acrylonitrile) and poly(vinyl alcohol) are described above. For example, useful spinning solvents for poly(vinyl alcohol) include aliphatic and aromatic alcohols of the desired 35 non-volatility and solubility for the polymer such as

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hydrocarbon polyols and alkylene ether polyols having a boiling point (at 101 kPa) between about 150°C and about 300°C, such as ethylene glycol, propylene glycol, glycerol, diethylene glycol and trimethylene glycol.

- 5 Suitable spinning solvents for polyolefins such as poly(ethylene) are hydrocarbons such as decalin, mineral oil, poly(ethylene) waxes and mixtures thereof.

The solvent is preferably mineral oil. The polymer may be present in the first solvent at a first
10 concentration which is preferably selected from a relatively narrow range, e.g. 2 to 15 weight percent, preferably 4 to 10 weight percent; however, once chosen, the concentration should not vary adjacent to the die or otherwise prior to cooling to the second
15 temperature. The concentration should also remain reasonably constant over time (i.e. length of the fiber or film).

The temperature of the spinning solvent is chosen to achieve complete dissolution of the polymer in the
20 first solvent. The temperature of the spinning solution is the preferably minimum temperature at any point between where the solution is formed and the die face, and must be greater than the gelation temperature for the polymer in the solvent at the first
25 concentration. For poly(ethylene) in mineral oil at 5 to 15% concentration; the gelation temperature is approximately from about 100°C to about 130°C. Therefore, a preferred spinning temperature for polyethylene in this solvent is from about 180°C to
30 about 250°C, and more preferably from about 200°C to about 240°C. Similarly, for poly(vinyl alcohol) in glycerine at about 5 to about 15% concentration, the gelation temperature is approximately 25 to about 100°C. Therefore, a preferred spinning temperature for
35 poly(vinyl alcohol) is between about 130°C and about

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250°C, more preferably between about 170 and about 230°C. While temperatures may vary above the spinning temperature at various points upstream of the die face, excessive temperatures causative of polymer degradation should be avoided. To assure complete solubility, a spinning temperature is chosen whereat the solubility of the polymer exceeds the first concentration and is typically at least about 20% greater. The gelation temperature is chosen whereat the first solvent-polymer system behaves as a gel, i.e., the system has a yield point and reasonable dimensional stability for subsequent handling. Cooling of the extruded polymer solution from the spinning temperature to the gelation temperature is preferably accomplished at a rate sufficiently rapid to form a gel fiber which is of substantially the same polymer concentration as existed in the polymer solution. Preferably the rate at which the extruded polymer solution is cooled from the spinning temperature to the second temperature is preferably at least 50°C per minute.

A preferred means of rapid cooling to the gelation temperature involves the use of a quench bath containing a liquid into which the extruded polymer solution falls after passage through an air gap (which may be an inert gas). Normally, however, the quench liquid and the first solvent have only limited miscibility. For example, in the case of the preferred poly(vinyl alcohol) fiber where the spinning solvent is preferably glycerol, the quench liquid is preferably a liquid such as paraffin oil. Similarly, for the preferred poly(acrylonitrile) fiber where the spinning solvent is preferably dimethyl sulfoxide suitable quenching solvent is preferably a liquid such as a mixture of water and dimethyl sulfoxide. In the case of the most preferred poly(ethylene fiber), there the

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spinning solvent is preferably a hydrocarbon (preferably mineral oil), the quench liquid is preferably water.

The preferred polyether solvents used as
5 extracting solvents in this invention may also function as quenching liquids. For example, where the spinning solvent is substantially soluble in the extraction solvent at elevated temperature but insoluble at lower temperatures, the spun fiber can be quenched by
10 contacting the spun fiber with the solvent at a lower temperature where the spinning solvent is insoluble in the polyether solvent and a temperature sufficiently low to quench the spun fiber. Thereafter, the fiber may be contacted with the solvent at elevated
15 temperature to extract the spinning solvent.

Some stretching during cooling to the gelation temperature at which a gel forms is not excluded from the present invention, but the total stretching during this stage should not normally exceed 10:1. As a
20 result of those factors, the gel fiber formed upon cooling to the second temperature consists of a continuous polymeric network highly swollen with a solvent.

If an aperture of circular cross section (or other
25 cross section without a major axis in the plane perpendicular to the flow direction more than 8 times the smallest axis in the same plane, such as oval, Y- or X-shaped aperture) is used, then both gels will be gel fibers, the xerogel will be an xerogel fiber and
30 the thermoplastic article will be a fiber. The diameter of the aperture is not critical, with representative apertures being between 0.25 mm and 5 mm in diameter (or other major axis). The length of the aperture in the flow direction should normally be at
35 least 10 times the diameter of the aperture (or other

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similar major axis), preferably at least 15 times and more preferably at least 20 times the diameter (or other similar major axis).

If an aperture of rectangular cross section is used, then both gels will be gel films, the xerogel will be a xerogel film and the thermoplastic article will be a film. The width and height of the aperture are not critical, with representative apertures being between about 2.5 mm and about 2 m in width (corresponding to film width), between about 0.25 mm and about 5 mm in height (corresponding to film thickness). The depth of the aperture (in the flow direction) should normally be at least about 10 times the height of the aperture, preferably at least about 15 times the height and more preferably at least about 20 times the height.

The extraction step is carried out at a first temperature at which the spinning solvent is soluble in the extracting solvent. The extent to which the spinning solvent is soluble in the extracting solvent may vary widely, the only requirement is that the solubility is such that the spinning solvent is extracted from the fiber to the desired extent at the first temperature. The first temperature employed will vary widely depending on the choice of spinning solvent and extracting solvent. For example, when the spinning solvent is a hydrocarbon such as mineral oil and the extracting solvent is a mono alkyl or dialkyl ether of polyalkylene glycol having alkyl groups of from 1 to about 5 carbon atoms and having alkylene and polyalkylene glycol groups where individual alkylene moieties include from about 2 to about 6 carbon atoms, such as diethylene glycol monobutyl ether and diethylene glycol monopropyl ether, first temperatures are preferably from about 55°C to about 100°C, more

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preferably from about 65°C to about 100°C and most preferably from about 75°C to about 100°C

After the spinning solvent has been extracted to the desired extent (preferably less than about 15 % by wgt., more preferably less than about 5.0 % by wgt. and most preferably less than about 1.5 % by wgt of the fiber), the extracted fiber is dried using conventional drying techniques, if the extraction solvent is sufficiently volatile. However, if the extracting solvent is not sufficiently volatile, the fiber may be extracted with a washing solvent which is more volatile than the extracting solvent and which is miscible with the extracting solvent. Washing replaces the extracting solvent in the gel with the more volatile washing solvent. Suitable washing solvents include water, low molecular weight alcohols such as methanol and ethanol, low molecular weight ethers such as dimethyl ether, methyl ethyl ether, dioxane, and tetrahydrofuran, and ketones such as acetone and methyl ethyl ketone. With the preferred polyether solvents, water is the preferred washing solvent primarily for convenience.

Once the fibrous structure containing the washing or extraction solvent is formed, it is then dried under conditions where the washing or extraction solvent is removed leaving the solid network of polymer substantially intact. By analogy to silica gels, the resultant material is called herein a "xerogel" meaning a solid matrix corresponding to the solid matrix of a wet gel, with the liquid replaced by gas (e.g. by an inert gas such as nitrogen or by air). The term "xerogel" is not intended to delineate any particular type of surface area, porosity or pore size.

Stretching may be performed upon the gel fiber after cooling to a temperature equal to or less than

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the gelation temperature or during or after extraction. Alternatively, stretching of the xerogel fiber may be conducted, or a combination of gel stretch and xerogel stretch may be performed. The stretching may be
5 conducted in a single stage or it may be conducted in two or more stages. The first stage stretching may be conducted at room temperatures or at an elevated temperature. Preferably the stretching is conducted in two or more stages with the last of the stages
10 performed at a temperature between 120°C and 150°C. Most preferably the stretching is conducted in at least two stages with the last of the stages performed at a temperature between 130°C and 150°C. Such temperatures may be achieved with heated tubes or with other heating
15 means such as heating blocks or steam jets.

After extraction, the solution containing the second extraction solvent and the first spinning solvent is preferably treated such that the two solvents are separated and the spinning solvent
20 recycled to the solution making step and the second extraction solvent recycled to the extraction step. Methods of separating the solution into the first and second portions may vary widely and any conventional procedure may be used as for example the procedure of
25 USP No. 4,334,102. In one preferred embodiment of the invention the spinning solvent and the second extraction solvent are separated by solvent extraction of the second extraction solvent from the solution with a third extraction solvent. For example, where the
30 second extraction solvent is a polyether such as triethylene glycol, triethylene glycol dimethyl ether, diethylene glycol diethyl ether, tetraethylene glycol dimethyl ether, or diethylene glycol dimethyl ether, the first spinning solvent and the second extraction
35 solvent are separated by extraction of the second

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extraction solvent from the solution with a third extraction solvent which is a solvent for the second extraction solvent and a non-solvent for the first spinning solvent forming a heterogeneous mixture of two liquid phases, one liquid phase being predominantly the first spinning solvent and the other liquid phase being a solution comprising said second and third extraction solvent. The first portion containing predominately the first spinning solvent (generally, at least 80 vol., preferably at least 90%, more preferably at least about 95 vol. and most preferably at least about 99 vol. by weight of the portion) can be recycled to form polymer fiber spinning solution.

Liquids useful as the third extraction solvent may vary widely provided that they provide this function. Preferred third extraction solvents are those which may be separated from the second extraction solvent by some suitable solvent separation technique which incorporates the lower critical solution temperature properties of said second and third extracting solvents, e.g. diethyl carbitol and water temperature-induced phase separation, and also including distillation, extraction, and the like to allow for recycling of the second extraction solvent to the first spinning solvent extraction step. More preferred third extraction solvents are those which can be separated from the second extraction solvent by distillation. Such third extraction solvents will usually have a boiling point at least about 80°C, preferably at least about 110°C, more preferably at least about 150°C less than that of the second extraction solvent. Illustrative of such preferred third extraction solvents are water, an alcohol such as ethanol, methanol and the like. More preferred third extraction solvents are water and alcohols, and the

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most preferred third extraction solvent is water.

Mixture of the second and third extraction solvents are separated through use of a suitable separation technique (as for example, those described above), such that the level of third extraction solvent in the second extraction solvent is such that the second extraction solvent is of sufficient purity to be recycled to the first spinning solvent extraction step. Likewise, the level of the second extraction solvent in the third extraction solvent is such that the third extraction solvent is of sufficient purity to be recycled to the extraction step involving the separation of first spinning solvent from second extraction solvent. After separation, the second extraction solvent can be directly recycled to the fiber extraction step or recycled subject to further optional treatment as for example drying with some drying agent as for example molecular sieves the third extraction solvent can be recycled to the second extraction solvent extraction step.

In another preferred embodiment of the invention, the second extraction solvent and first spinning solvent can be separated by change in temperature. For example, the solution of second extraction solvent and spinning solvent originally at the first temperature at which the two solvents are mutually soluble is heated or cooled to a temperature where the solvents are immiscible to form a heterogeneous two phase liquid system. One phase is a first phase comprising predominantly the spinning solvent and the other phase is a second phase comprising predominantly the extracting solvent. In general, the concentration of the predominant solvent in each phase is generally at least about 80%, preferably at least about 90%, more preferably at least about 95% and most preferably at

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least 99% by wgt of the phase.

The extent to which the spinning solvent is soluble in the extracting solvent may vary widely, the only requirement is that the solubility is such that
5 the spinning solvent and the extracting solvent can be separated to the desired extent at the second temperature. The second temperature employed in any particular extraction will vary widely depending on the choice of spinning solvent and extracting solvent. For
10 example, when the spinning solvent is a hydrocarbon such as mineral oil and the extracting solvent is a monoalkyl or dialkyl ether of a polyalkylene glycol having alkyl groups of from 1 to about 5 carbons and having alkylene and polyalkylene glycol groups where
15 individual alkylene moieties include from about 2 to about 6 carbon atoms, such as diethylene glycol monobutyl ether and diethylene glycol monopropyl ether, second temperatures are preferably from about 0°C to about 45°C, more preferably from about 0°C, to about
20 30°C and most preferably from about 0°C to about 25°C.

The spinning solvent phase containing less than about 20% by wgt, preferably less than about 10% by wgt, more preferably less than about 5% by wgt and most preferably less than about 2% by wgt of the phase of
25 the extracting solvent, and the extracting solvent phase preferably containing less than about 2 % by weight of the spinning solvent can be recycled to the solution forming step and extraction step, respectively. If the desired levels for recycling are
30 not achieved, the equilibrium can be shifted by the addition of a minor (1-2%) third component (e.g. water) to the hot solution comprised of the spinning solvent and the extracting solvent. If on initial temperature promoted phase separation, the required minimum
35 concentration levels still are not achieved, the

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various phases can be subjected to various other purification procedures such as distillation, solvent extraction and the like to reduce the amount of the minor component to the required levels.

5 Fibers prepared in accordance with the process of this invention can be used for conventional purposes for which fibers are used using conventional fiber processing techniques. For example, where the fibers formed from ultra high molecular weight linear
10 polyethylene, such fibers can be used in the fabrication of impact resistant articles as for example those described in U.S. Patent Nos. 4,916,000; 4,623,574; 4,403,012; 4,457,985; 4,457,985; 4,650,710; 4,681,792; 4,737,401; 4,543,286; 4,563,392 and
15 4,501,856.

The following examples are presented to more particularly illustrate the invention and are not to be construed as limitation thereon.

20 EXAMPLE I

The drawing illustrates in schematic form a first embodiment of the present invention, wherein the stretching step I is conducted in two stages on the xerogel fiber subsequent to drying step 4. In Figure
25 1, a first mixing vessel 10 is shown, which is fed with an ultra high molecular weight polymer 11 such as polyethylene of weight average molecular weight at least 500,000 and frequently at least 750,000, and to which is also fed mineral oil via fed line 12. First
30 mixing vessel 10 is equipped with an agitator 13. The residence time of polyethylene and mineral oil in first mixing vessel 10 is sufficient to form a slurry containing some dissolved polyethylene and some relatively finely divided polyethylene particles, which
35 polyethylene/mineral oil slurry is removed in line 14

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to an intensive mixing vessel 15. Intensive mixing vessel 15 is equipped with helical agitator blades 16. The residence time and agitator speed in intensive mixing vessel 15 is sufficient to convert the poly ethylene/mineral oil slurry into a solution. It will be appreciated that the temperature in intensive mixing vessel 15, either because of external heating, heating of polyethylene/mineral oil slurry 14, heat generated by the intensive mixing, or a combination of the above is sufficiently high (e.g. 200°C) to permit the polyethylene to be completely dissolved in the mineral oil at the desired concentration (generally between 5 to 10 percent polyethylene by weight of solution). From the intensive mixing vessel 15, the solution is fed to an extrusion device 18, containing a barrel 19 within which is a screw 20 operated by motor 22 to deliver the polyethylene solution at reasonably high pressure to a gear pump and housing 23 at a controlled flow rate. A motor 24 is provided to drive gear pump 23 and extrude the polyethylene solution, still hot, through a spinnerette 25 comprising a plurality of apertures, which may be circular, X-shaped, or, oval-shaped, or in any of a variety of shapes having a relatively small major axis in the plane of the spinnerette when it is desired to form fibers, and having a rectangular or other shape with an extended major axis in the plane of the spinnerette when it is desired to form films. The temperature of solution in the mixing vessel 15, in extrusion device 18 and at spinnerette 25 should all equal or exceed a first temperature (e.g. 200°C) chosen to exceed the gelation temperature (approximately 100-130°C) for polyethylene in mineral oil.

The temperature may vary (e.g. 220°C, 210°C and 220°C) or may be constant (e.g. 190°C) from the mixing

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vessel 15 to extrusion device 18 to the spinnerette 25. At all points, however, the concentration of polyethylene in the solution should be substantially the same. The number of apertures, and thus the number of fibers formed, is not critical, with convenient numbers of apertures being 16, 120, 240.

From the spinnerette 25, the polyethylene solution passes through an air gap 27, optionally enclosed and filled with an inert gas such as nitrogen, and optionally provided with a flow of gas to facilitate cooling. A plurality of gel fibers 28 containing mineral oil pass through the air gap 27 and into a quench bath 30 containing any of a variety of liquids, so as to cool the fibers, both in the air gap 27 and in the quench bath 30, to a second temperature at which the solubility of the polyethylene in the mineral oil is relatively low, such that the polyethylene/mineral oil system solidifies to form a gel. It is preferred that the quench liquid in quench bath 30 be water. While some stretching in the air gap 27 is permissible, it is preferably less than about 10:1.

Rollers 31 and 32 in the quench bath 30 operate to feed the fiber through the quench bath, and preferably operate with little or no stretch. In the event that some stretching does occur across rollers 31 and 32, some mineral oil exudes out of the fibers and can be collected as a top layer in quench bath 30.

From the quench bath 30, the cool first gel fibers 33 pass to a solvent extraction device 37 where an extraction solvent is fed through line 38 and is maintained in device 37 at a third temperature, T_3 . The extraction solvent is a polyether solvent which is a solvent for mineral oil at a third temperature, T_3 , but is a non-solvent for mineral oil at a fourth temperature, T_4 . The extraction solvent is also a

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solvent for water and is a non-solvent for polyethylene. The extraction solvent is preferably diethylene glycol monobutyl ether. The extraction solvent extracts the mineral oil spinning solvent from the gel fiber forming a fibrous structure containing less than about 1.5 % by weight of mineral oil based on the weight of the fiber. Solvent outflow line 40 contains solution of the polyether extraction solvent and the mineral oil spinning solvent at a third temperature, T_3 , at which the extraction solvent and spinning solvent are mutually soluble. The solution is conveyed via line 40 to solvent separator 41, where the solution is cooled to a fourth temperature at which the extraction solvent is substantially which causes the solution to separate into a phase rich in mineral oil and a phase rich in the polyether extraction solvent. Spinning solution phase is conveyed to mixer 10 by way of lines 42 and 11, and extraction solvent phase is conveyed to solvent extraction device 37 via lines 43 and 38.

Fibrous structure 44 which is conducted out of solvent extraction device 37 contains substantially only the extracting solvent and relatively little mineral oil. The fibrous structure 44 may have shrunken somewhat compared to the just gel fibers 33. Fibrous structure 44 is then conveyed to washing chamber 45 where structure 44 containing the extraction solvent is washed with a washing solvent in which the extraction solvent is soluble to remove the extraction solvent from structure 44. The washing solvent has a volatility of more than that of the extraction solvent (boiling point less than about 100°C. Preferred washing solvents are low molecular weight alcohols such as methanol and ethanol, and water. The preferred washing solvent is water. Structure 44 is washed for a

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time sufficient to remove up to 95% by wgt, preferably up to 99% by wgt, more preferably up to 99.8% by wgt based on the original concentration of the extracting solvent) of the extraction solvent from structure 44.

- 5 The solution of the washing solvent and the extraction solvent is conveyed to solvent recovery unit 46 by way of line 47 where the washing solvent and extraction solvent are separated. The washing solvent is returned to washing chamber 45 by way of line 48 and extraction
10 solvent is returned to extraction device 37 by way of line 49. Additional extraction solvent and washing solvent can be introduced into the system by way of line 66.

- Washed fibrous structure 50 is conveyed to drying
15 device 51. In drying device 51 the washing solvent is evaporated from the fibrous structure 50, forming essentially unstretched xerogel fibers 52 which are taken up on spool 53.

- From spool 53, or from a plurality of such spools
20 if it is desired to operate the stretching line at a slower feed rate than the take up of spool 53 permits, the fibers are fed over driven feed roll 54 and idler roll 55 into a first heated tube 56, which may be rectangular, cylindrical or other convenient shape.
25 Sufficient heat is applied to the tube 56, which may be rectangular, cylindrical or other convenient shape. Sufficient heat is applied to the tube 56 to cause the fiber temperature to be between 120-140°C. The fibers are stretched at a relatively high draw ratio (e.g.
30 5:1) so as to form partially stretched fibers 57 taken up by driven roll 58 and idler roll 59. From rolls 58 and 59, the fibers are taken through a second heated tube 60, heated so as to be at somewhat higher temperature, e.g. 130-160°C and are taken up by driven
35 take-up roll 61 and idler roll 62, operating at a speed

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sufficient to impart a stretch ratio in heated tube 60 as desired, e.g. 1.8:1. The twice stretched fibers 63 produced in this first embodiment are taken up on take-up spool 64.

5 With reference to the nine process steps of the present invention, it can be seen that the solution forming step A is conducted in mixers 13 and 15. The extruding step B is conducted with devices 18 and 23, and especially through spinnerette 25. The cooling
10 step C is conducted in airgap 27 and quench bath 30. Extraction step D is conducted in solvent extraction device 37. Extraction solvent and spinning solvent separation step E is conducted in separation 41. Fiber washing step F is conducted in washing chamber 45.
15 Washing solvent and extraction solvent recovery step G is carried out in solvent recovery unit 46. Drying step H is conducted in drying device 51. Stretching step I is conducted in elements 53-64 and especially in heated tubes 56 and 60. It will be appreciated,
20 however, that various other parts of the system may also perform some stretching, even at temperatures substantially below those of heated tubes 56 and 60. Thus, for example, some stretching (e.g. 2:1) may occur within quench bath 30, within solvent extraction device
25 37, within washing unit 45, within drying device 51 or between solvent extraction device 37 and drying device 51.

EXAMPLE II

30 A sample of gel spun SPECTRA® fiber (10.3230 gm, ca. 76% mineral oil) was extracted with a 50 gm of diethylene glycol monobutyl ether at 50°C for thirty minutes with periodic agitation. This process was repeated twice more. The fiber was then rinsed four times with ambient temperature (23-24°C) water
35 minutes each stage) and dried at 110°C in a vacuum oven

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for 15 minutes. The weight of the dried fiber was 2.9094 gm. The residual oil in the fiber was determined to be 0.15 wt % by IR analysis.

5

EXAMPLE III

A sample of gel spun SPECTRA® fiber (9.9768 gm, ca. 76% mineral oil) was extracted with 50 gm of diethylene glycol monobutyl ether at 75°C for thirty minutes with periodic agitation. This process was repeated twice more. The fiber was then rinsed four times with ambient temperature (23-24°C) water (15 minutes each stage) and dried at 110°C in a vacuum oven for 15 minutes. The weight of the dried fiber was 2.5338 gm. The residual oil in the fiber was determined to be 0.43 wt % by IR analysis.

15

EXAMPLE IV

A sample of gel spun SPECTRA™ fiber (10.1228) gm, ca. 76% mineral oil) was extracted with 50 gm of diethylene glycol monobutyl ether at 100°C for thirty minutes with periodic agitation. This process was repeated twice more. The fiber was then rinsed four times with ambient temperature (23-24°C) water (15 minutes each stage) and dried at 110°C in a vacuum oven for 15 minutes. The weight of the dried fiber was 2.4337 gm. The residual oil in the fiber was determined to be 0.00 wt % by IR analysis.

25

Using the procedure of Examples II to IV extractions were performed for polyether solvents at various temperatures. The residual mineral oil was determined by IR analysis. The results and process parameters (i.e. solvent at temperature) are set forth in the following Table I.

30

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TABLE I

	Solvent	Temp.	wt. % Residual Mineral Oil
5	Diethylene glycol monopropyl ether	50	11.3
	Diethylene glycol monopropyl ether	75	1.4
10	Diethylene glycol monopropyl ether	100	0
	Diethylene glycol t-butyl methyl ether	50	0
	Tetraglyme	50	46.0
	Tetraglyme	75	5.7
15	Tetraglyme	100	<0.2
	Triglyme	50	7.9
	Triglyme	75	0.66
	Triglyme	100	0
	Diglymee	50	0
20	Poly(propylene glycol) Mw=425	75	15.7
	Poly(propylene glycol) Mw=425	100	7.9

EXAMPLE V

25 The drawing illustrates in schematic form an
 embodiment of the present invention, wherein a first
 mixing vessel 10 is shown, which is fed with an ultra
 high molecular weight polymer 11 such as polyethylene
 of weight average molecular weight at least 500,000 and
 30 frequently at least 750,000, and to which is also fed
 mineral oil via fed line 12. First mixing vessel 10 is
 equipped with an agitator 13. The residence time of
 poly(ethylene) and mineral oil in first mixing vessel
 10 is sufficient to form a slurry containing some
 35 dissolved poly(ethylene) and some relatively finely
 divided poly(ethylene) particles, which

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poly(ethylene)/mineral oil slurry is removed in line 14 to an intensive mixing vessel 15. Intensive mixing vessel 15 is equipped with helical agitator blades 16. The residence time and agitator speed in intensive mixing vessel 15 is sufficient to convert the poly(ethylene)/mineral oil slurry into a solution. It will be appreciated that the temperature in intensive mixing vessel 15, either because of external heating, heating of polyethylene/mineral oil slurry 14, heat generated by the intensive mixing, or a combination of the above is sufficiently high (e.g. about 200°C) to permit the poly(ethylene) to be completely dissolved in the mineral oil at the desired concentration (generally between 5 to 10 percent poly(ethylene) by weight of solution). From the intensive mixing vessel 15, the solution is fed to an extrusion device 18, containing a barrel 19 within which is a screw 20 operated by motor 22 to deliver the polyethylene solution at reasonably high pressure to a gear pump and housing 23 at a controlled flow rate. A motor 24 is provided to drive gear pump 23 and extrude the poly(ethylene) solution, still hot, through a spinnerette 25 comprising a plurality of apertures, which may be circular, X-shaped, or, oval-shaped, or in any of a variety of shapes having a relatively small major axis in the plane of the spinnerette when it is desired to form fibers, and having a rectangular or other shape with an extended major axis in the plane of the spinnerette when it is desired to form films. The temperature of solution in the mixing vessel 15, in extrusion device 18 and at spinnerette 25 should all equal or exceed a first temperature (e.g. about 200°C) chosen to exceed the gelation temperature (approximately about 100 to about 130°C) for poly(ethylene) in mineral oil.

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The temperature may vary (e.g. about 220°C, about 210°C and about 200°C) or may be constant (e.g. about 220°C) from the mixing vessel 15 to extrusion device 18 to the spinnerette 25. At all points, however, the concentration of polyethylene in the solution is preferably substantially the same. The number of apertures, and thus the number of fibers formed, is not critical, with convenient numbers of apertures being 16, 120, 240.

From the spinnerette 25, the poly(ethylene) solution passes through an air gap 27, optionally enclosed and filled with an inert gas such as nitrogen, and optionally provided with a flow of gas to facilitate cooling. A plurality of gel fibers 28 containing mineral oil pass through the air gap 27 and into a quench bath 30 containing any of a variety of liquids, so as to cool the fibers, both in the air gap 27 and in the quench bath 30, to a second temperature at which the solubility of the poly(ethylene) in the mineral oil is relatively low, such that the polyethylene/mineral oil system solidifies to form a gel. It is preferred that the quench liquid in quench bath 30 is water. While some stretching in the air gap 27 is permissible, it is preferably less than about 10:1.

Rollers 31 and 32 in quench bath 30 operate to feed the fiber through the quench bath, and preferably operate with little or no stretch. In the event that some stretching does occur across rollers 31 and 32, some mineral oil exudes out of the fibers and can be collected as a top layer in quench bath 30.

From quench bath 30, the cool first gel fibers 33 pass to a solvent extraction device 37 where a second extraction solvent is fed through line 38 and is maintained in device 37 at some temperature. The

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second extraction solvent is a polyether solvent which is a solvent for the first spinning solvent mineral oil. The second extraction solvent is also a solvent for water and is a non-solvent for poly(ethylene). The

5 second extraction solvent is preferably monoalkyl or alkyl ether of a polyalkylene glycol such as diethylene glycol diethyl ether. The second extraction solvent extracts the mineral oil spinning solvent from the gel fiber forming a fibrous structure containing less than

10 about 15.0% by weight of mineral oil by weight of the fiber, and more preferably less than about 1.5% by weight of mineral oil by weight of the fiber, and a first solution of the mineral oil first spinning solvent and the polyether second extracting solvent.

15 The solution is conveyed via solution out line 40 to solvent separator 41 where the solution is extracted with a third extraction solvent, preferably water, forming a heterogeneous liquid mixture comprising two liquid phases, a first phase comprising the spinning

20 solvent (at least about 80 wt %, preferably at least about 90 wt %, more preferably at least about 95 wt % and most preferably at least about 99 wt % by weight of the first phase), and a second phase comprising a solution of the second and third extraction solvents.

25 The immiscible phases are separated and the spinning solvent phase is conveyed to mixer 10 by way of lines 42 and 11. The second phase is conveyed to extraction solvent recovery device 46 by way of line 49 where the second and third extraction solvents are separated by

30 some suitable method as for example temperature induced phase separation, for example when the second extraction is diethylene glycol diethyl ether and the third extraction solvent is water. The separated second extraction solvent is conveyed to solvent

35 extraction device 37 via lines 43 and 38 and the third

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extraction solvent is conveyed to solvent separation 41 by way of line 49(a). Fibrous structure 44 which is conducted out of solvent extraction device 37 contains substantially only the extracting solvent and

5 relatively little mineral oil. The fibrous structure 44 may have shrunk somewhat compared to the first gel fibers 33. Fibrous structure 44 is then conveyed to washing chamber 45 where structure 44 containing the second extraction solvent is washed with a washing

10 solvent in which the second extraction solvent is soluble (such as the third extraction solvent) to remove the second extraction solvent from structure 44. The washing solvent preferably has a volatility of less than that of the extraction solvent (boiling point

15 preferably less than about 100°C). Preferred washing solvents are low molecular weight alcohols such as methanol and ethanol, and water. In the preferred embodiments of the invention, the washing solvent is the same liquid as the third extraction solvent. The

20 most preferred washing solvent is water.

Structure 44 is washed for a time and extent sufficient to remove up to about about 5% by wgt, preferably up to about 1% by wgt, more preferably up to about 0.2% by wgt of the second extracting solvent

25 (based on the original concentration of the second extracting solvent) from structure 44. Because in the preferred embodiments the washing solvent and the second extracting solvent are the same, the solution of the washing solvent and the third extraction solvent is

30 conveyed to solvent recovery unit 46 by way of line 47 where the washing solvent and extraction solvent are separated. After washing, the mixture comprised of washing solvent and second extracting solvent can be recycled to working chamber 45 one or more times by a

35 convenient means as for example a line (not depicted)

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until the concentration of second extracting solvent in the washing solvent is too high for effective removal of second extracting solvent from structure 44 and thereafter conveyed to unit 46. However, in those
5 embodiments of the invention where the washing solvent and the third extracting solvent are different, the solution is carried to a washing solvent second extracting solvent separation chamber (not depicted), where the solvents are separated and the washing
10 solvent conveyed to washing chamber 45 and the second extraction solvent conveyed to device 37 by some suitable means, as for example a line (not depicted).

Washed fibrous structure 50 is conveyed to drying device 51. In drying device 51, the washing solvent is
15 evaporated from the fibrous structure 50, forming essentially unstretched xerogel fibers 52 which are taken up on spool 53.

From spool 53, or from a plurality of such spools if it is desired to operate the stretching line at a
20 slower feed rate than the take up of spool 53 permits, the fibers are fed over driven feed roll 54 and idler roll 55 into a first heated tube 56. Sufficient heat is applied to the tube 56 to cause the fiber temperature to be between about 120 and about 140°C.
25 The fibers are stretched at a relatively high draw ratio (e.g. about 5:1) so as to form partially stretched fibers 57 taken up by driven roll 58 and idler roll 59. From rolls 58 and 59, the fibers are taken through a second heated tube 60, heated so as to
30 be at somewhat higher temperature, e.g. from about 130 to about 160°C and are taken up by driven take-up roll 61 and idler roll 62, operating at a speed sufficient to impart a stretch ratio in heated tube 60 as desired, e.g. about 1.8:1. The twice stretched fibers 63
35 produced in this first embodiment are taken up on take-

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up spool 64.

With reference to the ten process steps of the preferred embodiment of the present invention described in this example, it can be seen that the solution forming step A is conducted in mixers 13 and 15. The extruding step B is conducted with devices 18 and 23, and especially through spinnerette 25. The cooling step C is conducted in air gap 27 and quench bath 30. Extraction step D is conducted in solvent extraction device 37. Extraction solvent and spinning solvent separation step E is conducted in separation 41. Second and third extraction solvents separation step F is conducted in unit 46. Fiber washing step G is conducted in washing chamber 45. Washing solvent and extraction solvent recovery step H is carried out in unit 46 in the preferred embodiments where the washing solvent and third extracting solvent are the same. Drying step I is conducted in drying device 51. Stretching step J is conducted in elements 53-64 and especially in heated tubes 56 and 60. It will be appreciated, however, that various other parts of the system may also perform some stretching, even at temperatures substantially below those of heated tubes 56 and 60. Thus, for example, some stretching (e.g. 2:1) may occur within quench bath 30, within solvent extraction device 37, within washing unit 45, within drying device 51 or between solvent extraction device 37 and drying device 51.

EXAMPLE VI

A sample of gel spun SPECTRA® fiber (10.2211 gm, approximately 76% mineral oil) was extracted with 50 gm of diethyl carbitol at 50°C for thirty minutes with periodic agitation. This process was repeated twice more. The fiber was then rinsed four times with ambient temperature (23-24°C) water (15 minutes each

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stage) and dried at 110°C in a vacuum oven for 15 minutes. The weight of the dried fiber was 2.4572 gm. The residual oil in the fiber was determined to be 0.3 wt % by infrared analysis.

5

EXAMPLE VII

A sample of gel spun SPECTRA® fiber (10.4084 gm, approximately 76 % mineral oil) was extracted three times with 50 gm diethyl carbitol at room temperature for thirty minutes each. The fiber was rinsed four times with ambient temperature water, 15 minutes for each stage. The fiber was then dried in a vacuum oven for 15 minutes at 110°C. The weight of the dried fiber was 2.5091 gm. Residual mineral oil left in the fiber is 0.8 wt % by infrared analysis.

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WHAT IS CLAIMED IS:

1. A process for extracting a first spinning solvent from a solution spun fiber, said process comprises the steps of:

5 (a) extracting a continuous length of a fiber containing a first spinning solvent with a second extraction solvent for a sufficient contact time to form a solution of said extracted first spinning solvent and said second extraction solvent and a fiber
10 containing said extraction second solvent, which fiber is free or substantially free of said first solvent and of substantially indefinite length; wherein said second extraction solvent is selected from the group consisting of :

15 (i) a second extraction solvent in which said first spinning solvent is soluble or substantially soluble at a first temperature, T_1 , and is insoluble or substantially insoluble at a second temperature, T_2 , such
20 that said second extraction solvent is capable of extracting said first spinning solvent from said fiber at said first temperature, T_1 , to form a first solution comprising said first spinning solvent and
25 said second extraction solvent and such that on subjection of said first solution to said second temperature T_2 , a first heterogenous mixture is formed comprising two distinct liquid phases, a first liquid phase
30 comprising predominantly said first spinning solvent and a second liquid phase comprising predominantly said second extraction solvent; and

35 (ii) a second extraction solvent in which said first spinning solvent is soluble or

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substantially soluble, which second extraction solvent is soluble or substantially soluble in a third extraction solvent which is immiscible in said first spinning solvent, said relative solubility of said second extraction solvent in said first spinning solvent and in said third extraction solvent being such that said third extraction solvent is capable of extracting all or a portion of said second extraction solvent from a second solution comprising said second extraction solvent and said spinning solvent to form a second heterogeneous liquid mixture comprising two distinct liquid phases, a third liquid phase comprising predominantly said first spinning solvent and a fourth liquid phase comprising predominantly said second extraction solvent and said third extraction solvent;

(b) separating said first solution or said second solution into said first and second liquid phases by subjecting said first solution to said second temperature, T_2 , for a time sufficient to form said first heterogeneous mixture or by extracting said second solution with said third extraction solvent for a time sufficient to form said second heterogeneous liquid mixture; and

(c) recycling said second phase or said fourth phase to said extraction step.

2. An improved process for solution spinning of polymeric fibers of the type which comprises the steps of forming a spinning solution of a polymer of fiber forming molecular weight and a spinning solvent; extruding said solution through an aperture, said solution being at a spinning temperature upstream of

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said aperture which is greater than the gelation temperature at which a rubbery gel is formed and being substantially at the first concentration both upstream and downstream of said aperture; cooling the solution adjacent to and downstream of the aperture to a gelation temperature below the temperature at which a rubbery gel is formed, forming a gel containing solvent of substantially indefinite length; extracting the gel containing first solvent with a second, volatile solvent for a sufficient contact time to form a fibrous structure containing second solvent, which gel is substantially free of first solvent and is of substantially indefinite length; drying the fibrous structure containing second solvent to form a xerogel of substantially indefinite length free of first and second solvent; and stretching at least one of, the gel containing the first solvent, the fibrous structure containing the second solvent and, the xerogel; said improvement comprising the steps of:

(a) extracting a continuous length of a fiber containing a first spinning solvent with a second extraction solvent for a sufficient contact time to form a solution of said extracted first spinning solvent and said second extraction solvent and a fiber containing said extraction second solvent, which fiber is free or substantially free of said first solvent and of substantially indefinite length; wherein said second extraction solvent is selected from the group (i)

a second extraction solvent in which said first spinning solvent is soluble or substantially soluble at a first temperature, T_1 , and is insoluble or substantially insoluble at a second temperature, T_2 , such that said second extraction solvent is capable of extracting said first spinning solvent from said fiber at said first

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- temperature, T_1 , to form a first solution comprising said first spinning solvent and said second extraction solvent and such that on subjection of said first solution to said second temperature T_2 , a first heterogenous mixture is formed comprising two distinct liquid phases, a first liquid phase comprising predominantly said first spinning solvent and a second liquid phase comprising predominantly said second extraction solvent; and
- (ii) a second extraction solvent in which said first spinning solvent is soluble or substantially soluble, which second extraction solvent is soluble or substantially soluble in a third extraction solvent which is immiscible in said first spinning solvent, said relative solubility of said second extraction solvent in said first spinning solvent and in said third extraction solvent being such that said third extraction solvent is capable of extracting all or a portion of said second extraction solvent from a second solution comprising said second extraction solvent and said spinning solvent to form a second heterogeneous liquid mixture comprising two distinct liquid phases, a third liquid phase comprising predominantly said first spinning solvent and a fourth liquid phase comprising predominantly said second extraction solvent and said third extraction solvent;
- (b) separating said first solution or said second solution into said first and second liquid phases by subjecting said first solution to said second temperature, T_2 , for a time sufficient to form said

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first heterogeneous mixture or by extracting said second solution with said third extraction solvent for a time sufficient to form said second heterogeneous liquid mixture; and

5 (c) recycling said second phase or said fourth phase to said extraction step.

3. A process according to claim 2 wherein said fiber is a poly(ethylene) fiber having a molecular weight equal to or greater than about 500,000.

10 4. A process according to claim 3 wherein said first spinning solvent is a hydrocarbon and said second extraction solvent is a polyether solvent.

5. A process according to claim 4 wherein said spinning solvent is mineral oil.

15 6. A process according to claim 5 wherein said polyether is a mono and dialkyl ethers of polyalkylene glycols are selected from the group consisting of polyethylene glycol ethers and polypropylene glycol ethers of the formula:

20
$$R(OCH_2CH_2)_xOR' \text{ and } R(OCH_2CH(CH_3)_xOR'$$

wherein:

x is an integer from 1 to about 8; and

R and R' are the same or different and are hydrogen or alkyl having 1 to about 4 carbon atoms.

25 7. A process according to claim 6 comprising the steps of:

(a) contacting said fiber containing said first spinning solvent with said second polyether extraction solvent at said first temperature, T_1 , said second extraction solvent selected such that said first spinning solvent is soluble or substantially soluble in said second extraction solvent at said first temperature, T_1 , and is insoluble or is substantially insoluble in said second extraction solvent at said second temperature, T_2 for a time sufficient to extract

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all or a portion of said spinning solvent from said fiber, to form a fiber of indefinite length containing said second solvent and a solution of said extracted first spinning solvent in said second extraction

5 solvent;

(b) separating said fiber from said solution;

(c) subjecting said solution of said spinning solvent and said polyether extraction solvent to said second temperature, T_2 , to form a heterogeneous liquid mixture comprising two distinct liquid phases, a first liquid phase comprising predominantly said first spinning solvent and a second liquid phase comprising predominantly said second polyether extraction solvent;

(d) separating said first and second phases; and

15 (d) recycling said second liquid phase to said contacting step (a).

8. A process according to claim 7 wherein said mono- and dialkyl ethers of poly alkylene glycols are selected from the group consisting of tetraethylene glycol dimethyl ether, triethylene glycol dimethyl ether, diethylene glycol monobutyl ether and diethylene glycol mono propyl ether.

9. A process according to claim 6 comprising the steps of:

25 (a) extraction a continuous length of a fiber containing a first spinning solvent with a polyether second extraction solvent, said second extraction solvent selected such that said first spinning solvent is soluble or substantially soluble in said second extraction solvent and said second extraction solvent is soluble in a third extraction solvent which is immiscible in said spinning solvent, said relative solubility of said second extraction solvent in said spinning solvent and in said third extraction solvent
30 being such that said third extraction solvent is
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capable of extraction all or a portion of said second extraction solvent from a first solution of said second extraction solvent and said spinning solvent, said extraction of said first spinning solvent by said
5 second extraction solvent for a time sufficient to form a fibrous structure containing said second extraction solvent, which structure is free of or substantially free of said first spinning solvent and a first solution comprising said extracted first spinning
10 solvent and said second extraction solvent;

(b) extraction said first solution with said third extraction solvent for a time sufficient to form a heterogeneous liquid mixture comprising two distinct liquid phases, a first liquid phase comprising
15 predominantly said first spinning solvent and a second liquid phase comprising predominantly a second solution comprising said second extraction solvent and said third extraction solvent;

(c) separating said first and second phases of
20 step (b); and

(d) separating said second extraction solvent from said third extraction solvent and recycling said second extraction solvent to extraction step (a) and said third extraction solvent to extraction step (b).

25 10. An improved process according to claim 9 wherein said second extraction solvent is selected from the group consisting of dimethyl diethylene glycol and diethyl diethylene glycol and said third extraction solvent is water or an alcohol having from 1 to 4
30 aliphatic carbon atoms.

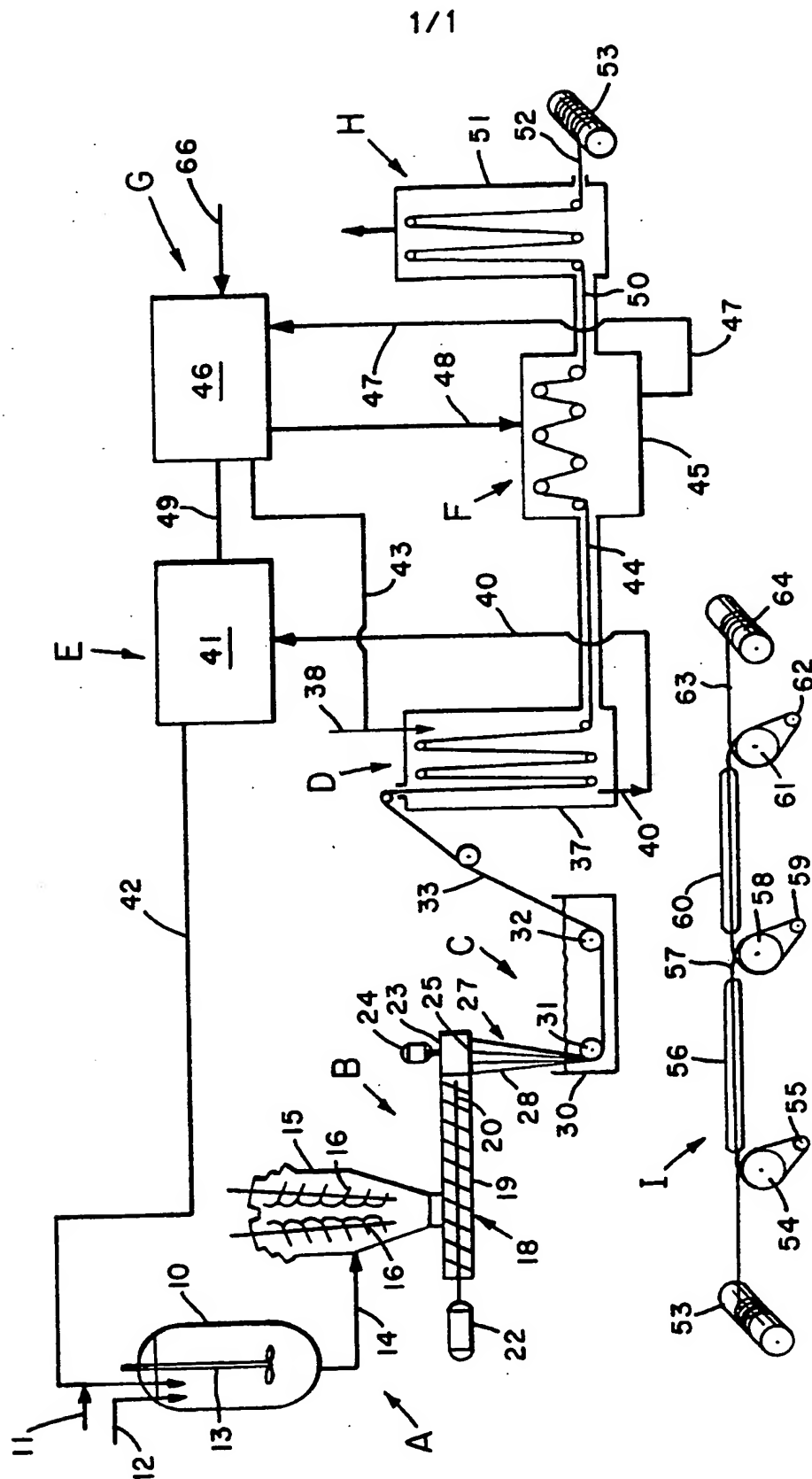


FIG. 1

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 92/10571

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 D01F13/04; D01F6/04		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	D01F	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	DE,B,1 052 057 (STOCKHOLMS SUPERFOSFAT FABRIKS AKTIEBOLAG) 5 March 1959 see the whole document ---	1,2
A	GB,A,1 214 540 (SOCIETA ITALIANA RESINE S.P.A.) 2 December 1970 see the whole document ---	1,2
A	EP,A,0 062 789 (BASF AG) 20 October 1982 see page 2, line 17 - page 3, line 29 see page 7, line 15 - page 8, line 4 ---	5,6,9,10
A	US,A,4 334 102 (WILMOT H. DECKER ET AL.) 8 June 1982 cited in the application see the whole document ---	5,6,9,10
-/--		
<p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
23 MARCH 1993	08.04.93	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	TARRIDA TORRELL J.B.	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	EP,A,0 064 167 (ALLIED CORPORATION) 10 November 1982 cited in the application -----	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9210571
SA 68028

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-B-1052057		BE-A- 524580 DE-B- 1124629 FR-A- 1074721 GB-A- 106154 GB-A- 706154 NL-C- 84821 NL-B- 174886	
GB-A-1214540	02-12-70	None	
EP-A-0062789	20-10-82	DE-A- 3112661 CA-A- 1178789 JP-A- 57174385 US-A- 4414004	14-10-82 04-12-84 27-10-82 08-11-83
US-A-4334102	08-06-82	None	
EP-A-0064167	10-11-82	US-A- 4413110 AU-B- 581702 AU-B- 549453 AU-A- 8225482 CA-A- 1174818 JP-A- 58005228 US-A- 4536536 US-A- 4551296	01-11-83 02-03-89 30-01-86 04-11-82 25-09-84 12-01-83 20-08-85 05-11-85

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